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(54) **MCrAlY type alloy coating**

(57) A gas turbine component consists of a super-alloy base material with a single crystal structure and a protective MCrAlY-coating (6). The MCrAlY-coating (6)

has a γ/γ' single crystal structure, which is epitaxial with the base material. It has be determined the critical factors for the successful epitaxial growth of the MCrAlY-coating (6).

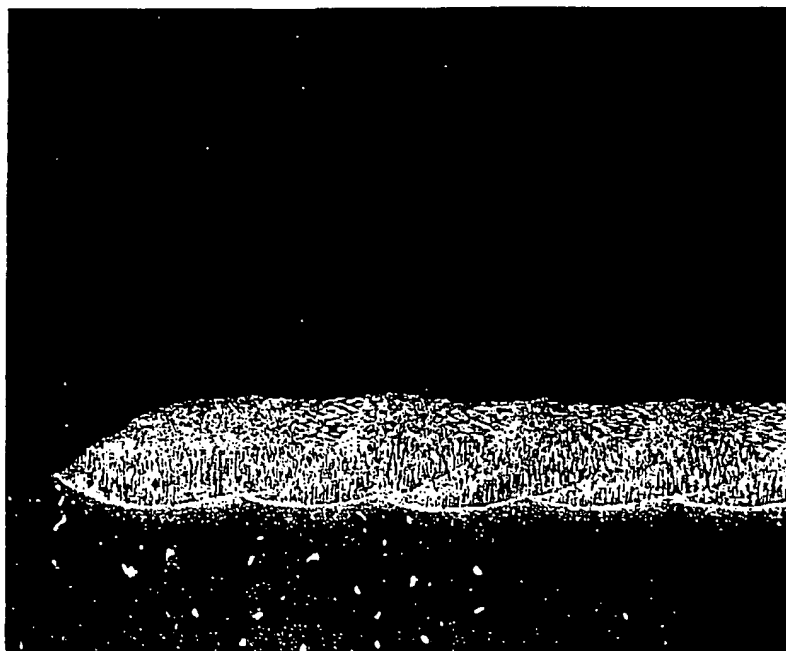


Fig. 2

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Description

FIELD OF INVENTION

- 5 [0001] The invention relates to a MCrAlY-coating according to the preamble of claim 1.

STATE OF THE ART

10 [0002] Components designed for the use in the area of high temperature, e.g. blades or vanes of a gas turbine, are usually coated with resistant coatings. The coating protects the base material against corrosion and oxidation due to the thermal effect of the hot environment and consists of an alloy mostly using the elements Al and Cr. Most turbine components are coated for the protection from oxidation and/or corrosion with, for example, a MCrAlY coating (base coat) and some are also coated with a thermal barrier coating (TBC) for thermal insulation. MCrAlY protective overlay coatings are widely known in the prior art. They are a family of high temperature coatings, wherein M is selected from one or a combination of iron, nickel and cobalt. As an example US-A-3,528,861 or US-A-4,585,481 are disclosing such kind of oxidation resistant coatings. US-A-4,152,223 as well discloses such method of coating and the coating itself. Besides the $\gamma\beta$ -MCrAlY-coating, there is another class of overlay MCrAlY coatings which are based on a $\gamma\gamma$ -gamma/gamma prime-structure. The advantages of $\gamma\gamma$ -coatings is that they have a negligible thermal expansion mismatch with alloy of the underlying turbine article. For higher thermal fatigue resistance the $\gamma\gamma$ -coating are more convenient compared to the $\gamma\beta$ -type of MCrAlY-coatings. A higher thermal fatigue resistance in coatings is most desirable since failure of the most turbine blades and vanes at elevated temperature is typically thermal fatigue driven.

20 [0003] Among $\gamma\gamma$ -coatings and $\gamma\beta$ -coatings, the field of $\gamma\beta$ -coatings have been an active area of research and a series of patents has been issued. E.g. a Ni-CrAlY coating is described in US-A-3,754,903 and a CoCrAlY coating in US-A-3,676,058. US-A-4,346,137 discloses an improved high temperature fatigue resistance NiCoCrAlY coating. US-A-4,419,416, US-A-4,585,481, RE-32,121 and US-A-4,743,514 describe MCrAlY coatings containing Si and Hf. US-A-4,313,760 discloses a superalloy coating composition with good oxidation, corrosion and fatigue resistance.

25 [0004] In contrast to the $\gamma\beta$ -coatings, the $\gamma\gamma$ -type of MCrAlY coatings, known e.g. from US-A-4,973,445, are relatively new. The unique feature of this type of $\gamma\gamma$ -coatings is that their thermal expansion mismatch is close to zero in combination with a high ductility, what make these coatings more resistant to thermal fatigue. However the limitations are the low aluminum content and hence their low reservoir of aluminum.

30 [0005] Furthermore, US-A-4,758,480 discloses a class of coatings whose composition is based on the composition of the underlying substrate. The similarity in phase structure and in the chemical composition renders the mechanical properties of the coating similar to those of the substrate thereby reducing thermomechanically-reduced damage during service. However, when this coating is applied by traditional means on the single crystal substrate, the difference in the E-modulus between $\langle 010 \rangle$ oriented surface layer of the substrate and randomly oriented coating grains produce high TMF damage.

35 [0006] US-A- 5,232,789 discloses the further improvement of the TMF properties of the coating-substrate system. The coating, which has composition and phase structure similar to the substrate alloy, has at least 1000 times more fine-grained structure, produced by a special technology. The lowermost interface portion of the fine-grained coating grows epitaxially, and therefore has the same crystal orientation as the substrate. Epitaxial growth solves also coating / substrate interface adhesion problem.

40 [0007] However, the system of a single crystal substrate and the multicrystal coating still has a large difference in the mechanical behavior between the substrate and the coating as any equiaxed structure possesses E-modulus much higher than those for single crystal material in $\langle 001 \rangle$ direction. Higher E-modulus reflects in lower TMF life of the coating compared to the substrate (although the stresses on substrate-coating interface are significantly reduced compared to the traditional coating - substrate system). Multiple grain boundaries drastically reduce the creep resistance of the fine-grain coating, which finally determines life of the entire blading system.

45 [0008] Therefore, in general, US-A-6,024,792 is disclosing a method for producing monocrystalline structures on substrates with monocrystalline structures by using an energy beam of high energy from an energy source. The material which is to be introduced into the monocrystalline structure is supplied to the melted region of the substrate. The supplied material is completely melted. An similar method is known from EP-A1-740 977.

50 [0009] More special, EP-A1-1 001 055 is disclosing a MCrAlY-coating and a method of depositing the coating, whereby the coating is epitaxially on the base material and the coating is grown with a single crystal structure. The coating is applied by laser cladding. It was found, in fact, that it was difficult to grown a defect free epitaxial coating with the mentioned $\gamma\gamma$ forming coating material within this document. When using other commercially available highly oxidation resistant alloys for the laser cladding process, the single crystal microstructure can not be maintained. Hot tearing cracks and the breakdown of single crystal solidification occur in the clad structure, which results in the formation of undesirable equiaxed grains.

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SUMMARY OF THE INVENTION

[0010] It is object of the present invention to find a γ/γ -MCrAlY-coating and to determine in detail the parameter of cladding a defect free, epitaxial coating on a single crystal article. The epitaxial coating is grown on the single crystal substrate, which means that it has the same crystallographic orientation as the substrate.

[0011] According to the invention a bond MCrAlY-coating according to the preamble of claim 1 was found, wherein the MCrAlY has a γ/γ -phase and wherein the MCrAlY comprises less than 1.2 wt.-% Si.

[0012] Another condition for advantageous embodiment the epitaxial solidification of the coating is that the solidification temperature interval ΔT_0 of the MCrAlY-coating is smaller than 30°C.

[0013] To obtain the γ/γ structure of the coating the last 5% of the MCrAlY-coating liquid must solidify in a temperature interval ΔT_1 smaller than 15°C.

[0014] Both factors, a small solidification interval and the last 5% of the liquid, here determines the width of the mushy zone, the narrower the mushy zone the lower is the susceptibility for hot tearing during the cladding process.

[0015] To obtain a small solidification interval ΔT_0 the composition of the MCrAlY-coating should be as close as possible to the eutectic line on the γ -phase side of the eutectic line of the ternary phase diagram Ni - Al - Cr.

[0016] As an example the MCrAlY-coating has the following composition (wt.-%) 18-26.0 % Cr, 5-8.0 % Al, 0.1-1.2 % Si, 0.4 - 1.2 % Y, 0 - 0.1 % Hf and 0.1 - 1.2% Ta, balance Ni and unavoidable impurities with $\Sigma(\text{Al} + \text{Si}) < 10\%$, $\Sigma(\text{Si} + \text{Ta}) < 2.5\%$, $\Sigma(\text{Y} + \text{Hf} + \text{Zr} + \text{La}) < 1.5\%$, C max. 0.03 %.

[0017] Advantageous to obtain a small solidification interval, the coating will comprise an addition of Si up to 0.5wt.-%, Hf up to 0.5wt.-%, Y below 0.5 wt.-%, Ta below 3 wt.-%

[0018] For increased oxidation resistance the coating may contain Fe, Ga, Mg, Ca individually or a combination thereof.

[0019] In an advantageous embodiment, the MCrAlY-coating is applied by laser cladding with a thickness of 100 to 300 μm and the article is a gas turbine component made of a nickel base super alloy.

BRIEF DESCRIPTION OF DRAWINGS

[0020] This invention is illustrated in the accompanying drawing, in which

Fig. 1 shows a schematic representation of a laser cladding process,

Fig. 2 shows an example of an epitaxially γ/γ -MCrAl-coating according to the invention and

Fig. 3 shows an example of a non epitaxially γ/γ -MCrAl-coating.

[0021] The drawings show only parts important for the invention.

DETAILED DESCRIPTION OF INVENTION

[0022] This invention is related to a method of epitaxially growing a MCrAlY-coating 6 having a γ/γ -microstructure onto a surface 5 of an article 4 such as blades or vanes of gas turbines or any other part which is exposed to a hot temperature environment. The article 4 has a single crystal (SX) structure and can be made, as an example, from a nickel base super-alloy. Nickel base superalloys are known in the state of the art, e.g. from the document US 5,888,451, US 5,759,301 or from US 4,643,782, which is known as "CMSX-4". In general, figure 1 shows a laser cladding process which is characterized by impinging particles of the MCrAlY-coating material with a powder jet 1 onto a molten pool 2 formed by controlled laser heating by scanning the laser beam 3 successively over the surface 5 of the single crystal article 4. The arrow 7 shows the direction of the movement over the article 4.

[0023] The laser cladding technology has been used to apply an epitaxial γ/γ -MCrAlY-coating 6 with 100 - 300 μm thickness on the single crystal superalloy article 4. The coating 6 is epitaxially grown on the article 4, which means that it has the same crystal orientation as the article 4.

[0024] It has been found that the following factors are critical for the successful epitaxial growth of the MCrAlY-coating 6. The solidification interval ΔT_0 of the coating 6 must be narrow. To obtain a small solidification interval ΔT_0 of the MCrAlY-coating the MCrAlY comprises less than 1.2 % Si. As an example the solidification interval ΔT_0 shall be 30°C and smaller. The solidification interval must be low to enable the growth of SX microstructure and to prevent hot tearing. The smaller ΔT_0 is the bigger the process window, which allows the SX growth without any equiaxed grain.

[0025] The MCrAlY coating 6 has a designed solidification interval ΔT_0 by alloying with a controlled amount of certain elements. The solidification interval ΔT_0 increases or decreases with the addition of the elements such as Si, Hf, Zr, Y, Ta. Furthermore, the SX-MCrAlY coating 6 design results in a chemical composition close to the eutectic line on the γ -phase side of the eutectic line of the phase diagram of nickel-chromium-aluminum ternary. The closer one gets to the eutectic line the narrower the solidification interval ΔT_0 . Here, ΔT_0 is mainly controlled by the Al content of the

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coating 6. The coating 6 may contain the elements Si, Hf and Zr and a small addition of Ta, Fe, Ga, Mg, Ca individually or a combination thereof as well for increased oxidation resistance.

[0026] A γ/γ -MCrAlY-coating 6 according to the invention can have the preferred range of following composition (wt. %): 18 - 26.0 % Cr, 5 - 8.0 % Al, 0.1 - 1.2 % Si, 0.4 - 1.2 % Y, 0-0.1 % Hf, 0.1 - 1.2 % Ta, balance Ni and unavoidable impurities with Σ (Al + Si) < 10 %, Σ (Si + Ta) < 2.5 %, Σ (Y + Hf + Zr + La) < 1.5 %, C max. 0.03%.

[0027] In addition, in an advantageous embodiment to obtain a favorable, low solidification interval ΔT_0 , the concentration of minor elements in the coating should be Si up to 0.5 wt.-%, Hf up to 0.5 wt.-%, Y below 0.5 wt.-% and Ta below 3 wt.-%.

[0028] The concentration of the minor elements such as Y, Zr and Ta must also be adjusted to prevent formation of brittle Ni (Ta, Si) phases containing these elements.

[0029] Another important factor is that the last 5% liquid should solidify in a ΔT_1 interval smaller than 15°C in order to prevent hot tearing. The ΔT_1 here determines the width of the mushy zone, the narrower the mushy zone the lower is the susceptibility for hot tearing during the cladding process.

[0030] The composition of the MCrAlY should be adjusted to avoid precipitation of Cr-rich sigma or any other undesirable phases. The brittle sigma phases are detrimental to the mechanical properties of the coating.

[0031] Examples of γ/γ -MCrAlY coating according to the invention are shown in table 1. (wt.-%)

Tab.1

Example	Ni	Cr	Al	Ta	Si	Y	ΔT_0 [°C]
I	Bal.	25	6	--	--	0.4	25
II	Bal.	16.5	5.5	--	--	0.4	25
SV20	Bal.	24	5	1	2.5	0.5	95

[0032] It is to be noted that the ΔT_0 of coatings I and II in table 1 is approximately 25°C, while the ΔT_0 of SV20 is 95°C. The coatings I and II can be deposited on a substrate as single crystal but not SV20. Since ΔT_0 of SV20 is much higher than 30°C, it is difficult to produce SV20 in single crystal form instead a mixture of single crystal and equiaxed structure is formed.

[0033] On the other hand, when the laser parameters e.g. such as laser power, scanning speed, protection gas are optimized and balanced against each other for the deposition of a SX-MCrAlY coating 6 onto a SX base material. The alloy design of the newly MCrAlY coating 6 supports the maintenance and growth of the SX coating.

[0034] The Example of Fig. 2 shows a result of a coating from this invention with a fully SX-structure and no cracks. The condition of the annexed claim have been fulfilled. The very even and parallel dendrite structure indicate the SX structure of the clad, which has been also proven with the Electron Back Scattering Diffraction (EBSD) Kikuchi technique.

[0035] In contradiction Fig. 3 shows an example of a non-epitaxially nucleation at the CMSX-4 substrate. Although clad with optimized Laser parameters the coating material was very difficult to apply. Outside of the rage of the conditions of the claims it is very susceptible to hot tearing and breakdown of SX structure.

REFERENCE NUMBERS

[0036]

- 1 powder jet
- 2 molten pool
- 3 laser beam
- 4 article
- 5 surface of article 4
- 6 coating
- 7 direction of movement

ΔT_0 Solidification interval of coating 6

ΔT_1 Solidification interval of last 5% liquid of coating 6

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Claims

1. An article (4) having a surface (5) and a single crystal structure, the article (4) coated with protective MCrAlY-coating (6), which MCrAlY is epitaxially grown on the surface (5) of the article (4), wherein the MCrAlY has a γ/γ' -structure and wherein the MCrAlY comprises less than 1.2 wt.-% Si.
2. The article (4) according to claim 1, wherein the MCrAlY-coating (6) has a solidification temperature interval (ΔT_0) of smaller than 30°C.
3. The article (4) according to claim 1, wherein the MCrAlY-coating (6) has a temperature interval (ΔT_1) of the last 5% liquid of smaller than 15°C.
4. The article (4) according to any of the claims 1 to 3, wherein the composition of the MCrAlY-coating (6) is close to the eutectic line on the γ -phase side of the eutectic line of the ternary phase diagram Ni - Al - Cr.
5. The article (4) according to claim 1, wherein the MCrAlY-coating (6) comprises the following composition (wt.-%) 18 - 26.0 % Cr, 5 - 8.0 % Al, 0.1 - 1.2 % Si, 0.4 - 1.2 % Y, 0 - 0.1 % Hf, 0.1 - 1.2% Ta, Balance Ni and unavoidable impurities with Σ (Al + Si) < 10 %, Σ (Si + Ta) < 2.5 %, Σ (Y + Hf + Zr + La) < 1.5 %, C max. 0.03 %.
6. The article (4) according to claim 1, wherein the MCrAlY-coating (6) comprises (wt.-%) Si up to 0.5 %, Hf up to 0.5 %, Y < 0.5 % and Ta < 3 % individually or a combination thereof.
7. The article (4) according to any of the claims 1 to 6, wherein the coating (6) comprises an addition of Fe, Ga, Mg, Ca individually or a combination thereof.
8. The article (4) according to any of the claims 1 to 7, wherein the coating (6) has a thickness of 100- 300 μ m.
9. The article (4) according to any of the claims 1 to 8, wherein the MCrAlY-coating (6) is applied by laser cladding.
10. The article (4) according to any of the claims 1 to 9, wherein it is a gas turbine component made from nickel base super alloy.

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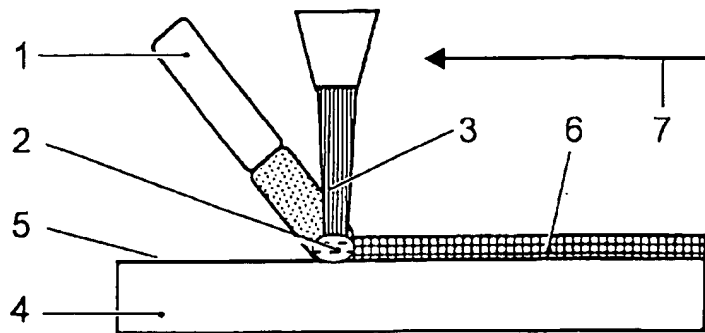


Fig. 1

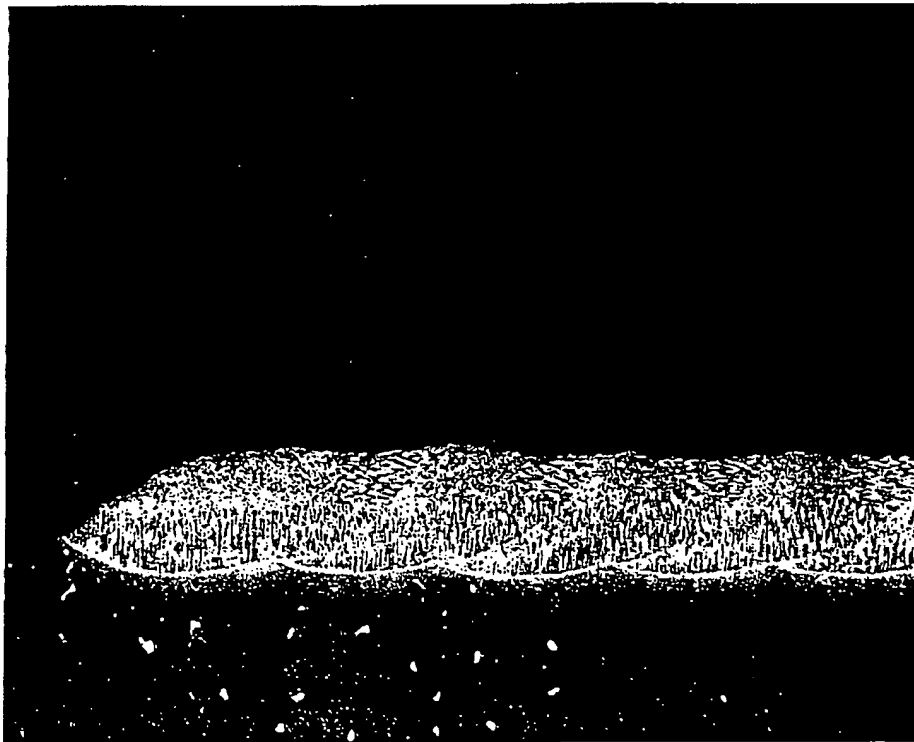


Fig. 2

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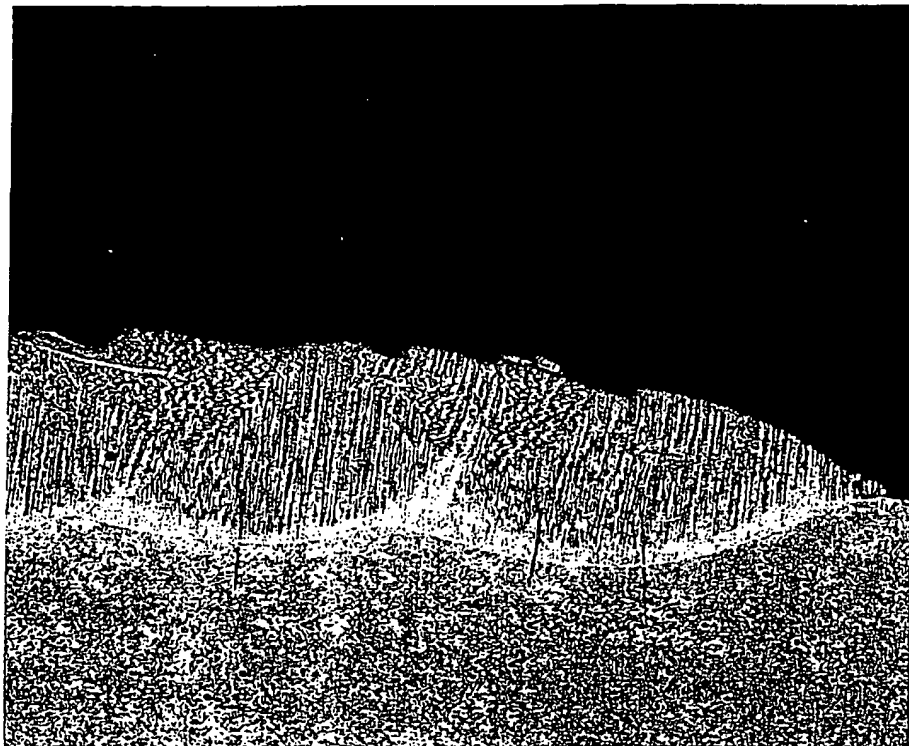


Fig. 3

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EUROPEAN SEARCH REPORT

Application Number

EP 01 12 2819

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Incl.7)
A,D	US 5 232 789 A (PLATZ ALBIN ET AL) 3 August 1993 (1993-08-03) * column 4; claims 1,3 *	1,5,10	C30B13/00 C30B29/52 C22C19/05
A,D	EP 1 001 055 A (ABB RESEARCH LTD) 17 May 2000 (2000-05-17) * page 3, line 29 - page 4, line 30; claims 1-9 *	1,5,8-10	
A,D	US 4 973 445 A (SINGHEISER LORENZ) 27 November 1990 (1990-11-27) * claims 1-3 *	1,5,10	
A,D	US 6 024 792 A (KURZ WILFRIED ET AL) 15 February 2000 (2000-02-15)		
A,D	US 4 743 514 A (STRANGMAN THOMAS E ET AL) 10 May 1988 (1988-05-10)		
A	US 5 993 980 A (SCHMITZ FRIEDHEIM ET AL) 30 November 1999 (1999-11-30)		
			TECHNICAL FIELDS SEARCHED (Incl.7)
			C30B C22C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 22 February 2002	Examiner Cook, S
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5232789 A	03-08-1993	DE 3907625 C1	15-02-1990
		CA 2011753 A1	09-09-1990
		EP 0386618 A1	12-09-1990
		JP 2277760 A	14-11-1990
EP 1001055 A	17-05-2000	EP 1001055 A1	17-05-2000
		US 6277500 B1	21-08-2001
US 4973445 A	27-11-1990	DE 3740478 C1	19-01-1989
		DE 3882024 D1	29-07-1993
		EP 0318803 A1	07-06-1989
US 6024792 A	15-02-2000	EP 0861927 A1	02-09-1998
		CA 2230323 A1	24-08-1998
		EP 0892090 A1	20-01-1999
US 4743514 A	10-05-1988	EP 0282667 A1	21-09-1988
		JP 63216982 A	09-09-1988
US 5993980 A	30-11-1999	DE 59505454 D1	29-04-1999
		WO 9612049 A1	25-04-1996
		EP 0786017 A1	30-07-1997
		JP 10507230 T	14-07-1998
		RU 2147624 C1	20-04-2000

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